LONG-TERM ENVIRONMENTAL EFFECTS OF OFFSHORE OIL AND GAS DEVELOPMENT

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CHAPTER 4

OFFSHORE OIL AND GAS DEVELOPMENT ACTIVITIES POTENTIALLY CAUSING LONG-TERM ENVIRONMENTAL EFFECTS

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INTRODUCTION

There often is much confusion about activities involved in offshore oil and gas development which might potentially result in adverse environmental effects. In the forefront of the minds of most people are, of course, large oil spills. Yet experience has shown that these occur rarely. Smaller accidental oil spills and discharges which are purposely made during normal operations are more pervasive. The regulation of operational discharges has come under increasing scrutiny in recent years. What exactly do they consist of, and how much is discharged? Finally, construction and transportation of equipment, materials and product are frequently not considered as causes of adverse environmental effects. What do they entail, and how might they affect the marine environment?

This chapter presents a description of activities involved in the exploration for and production of oil and gas in offshore environments. Special emphasis is placed on characterizing the nature and amount of discharges, both operational and accidental, based on recent experience. The chapter is intended as background and an information source for the chapters to follow, which will specifically consider the potential long-term effects of these activities. Excluded from this review, as they are from throughout the book, are those activities related to

SEQUENCE OF ACTIVITIES

The sequence of activities necessary for evaluation of the resource potential, exploration, development, production and refining of oil and gas from offshore regions are summarized in Table 4.1, together with an abbreviated description of their potential effects.

The first industrial activity which takes place on the continental shelf is geophysical surveying to evaluate the oil and gas resource potential based on evidence of sources, reservoirs and traps in the geological strata. This involves the pulsing of high intensity acoustic signals through the ocean and sedimentary strata. Although early use of explosives resulted in some destruction of marine life, current technology is thought to be safe for fishes and invertebrates. In any case, long-term effects are unlikely. Concern continues to be raised about the effects of seismic surveying on marine mammals, particularly cetaceans which communicate with an elaborate repertoire of acoustic signals.

Once the geophysical data indicate a potential for recoverable oil and gas resources and leases for drilling rights are obtained, the exploratory drilling phase may be entered. The mobile drilling rigs, including barges, jackups, drill ships and semisubmersibles, which are used for exploratory drilling offshore, are fabricated at coastal or inland shipyards, not necessarily in the region of the exploratory drilling. In fact, under present economic conditions, most new large mobile drilling rigs are constructed in Asia and Europe. Rigs are towed or move under their own power to the site of exploratory drilling and anchored at multiple mooring points (may be dynamically positioned in deeper waters).

Initial drilling into the seabed (spudding in) in order to place risers to the surface results in the direct discharge of sediment, cuttings and drilling fluids at the seafloor. Thereafter, recirculated drilling fluids, necessary to cool, lubricate and transport solids from the drill bit, are separated from cuttings (the pulverized formation) on the rig. The cuttings are usually discharged overboard continuously, while the drilling fluids are reused and disposed of later, again generally overboard at the drilling location. The composition of drilling fluids is discussed in detail below. In addition to drilling discharges, water drainage from the deck of the rig may contain drilling fluids, oil and small quantities of industrial chemicals used aboard the rig. Sanitary wastes are usually discharged at sea after treatment.

The transport of materials and men to the rig may be accomplished by vessel or aircraft. As a result of increased vessel traffic, discharges of oily and sanitary wastes may increase. Coastal ports may be expanded, and navigation channels constructed or deepened. Helicopters and fixed wing aircraft may disturb nesting or aggregating birds or mammals.

Because the probability of discovery of an economically viable resource is low for any given exploratory well, there is typically a sparse distribution and brief duration of operational discharges during exploration. In many frontier regions, this may be all that occurs. If highly pressured gas or oil strata are drilled, the possibility of a blowout exists, but redundant blowout preventers make this a

TABLE 4.1
Major activities in the development of an offshore oil and gas field and their potential effects on marine and coastal environments

Activity	Potential effects
Evaluation	
Seismic surveying	Noise effects on fishes and mammals
Exploration	
Rig fabrication	Dredging and filling of coastal habitats (mostly overseas)
Rig emplacement	Seabed disturbance due to anchoring
Drilling	Discharge of drilling fluids and cuttings; risk of blowouts
Routine rig operations	Deck drainage and sanitary wastes
Rig servicing	Discharges from support vessels and coastal port development
Development and production	
Platform fabrication	Land use conflicts and increased channelization in heavily developed areas
Platform installation	Coastal navigation channels, seabed disturbance resulting from placement and subsequent presence of platform
Drilling	Larger and more heavily concentrated discharges of drilling fluids and cuttings; risk of blowouts
Completion	Increased risk of oil spills
Platform servicing	Dredges and coastal port development; discharges from vessels
Separation of oil and gas from water	Chronic discharges of petroleum and other pollutants
Fabrication of storage facilities and pipelines	Coastal use conflicts
Offshore emplacement of storage and pipelines	Seabed disturbances; effects of structures
Transfer to tankers and barges	Increased risk of oil spills; acute and chronic inputs of petroleum
Construction of onshore facilities for transportation and storage	Coastal use conflicts; alterations of wetlands in pipeline corridors
Pipeline operations	Oil spills; chronic leaks
Refining	
Construction and expansion	Coastal use conflicts
Operations	Increased pollutant loading; depends on regional demands, imports, etc.

In case a discovery of promising oil or gas shows, further drilling from mobile drilling rigs to delineate the bearing reservoirs is usually necessary before recovery of the resource begins. Should these results warrant, a fixed platform may be placed from which several development wells may be drilled. In deeper waters, development drilling may take place from platforms which are not founded on

platform installation. In some nearshore locations, particularly in the Arctic, an artificial island will be built of sand or gravel to support drilling and production. Drilling of multiple wells from a fixed location will, of course, result in larger and more heavily concentrated discharges of drilling fluids and cuttings. The risk of oil spills may increase as the producing well is completed.

Fabrication of platforms may take place onshore nearby the well location (Gulf of Mexico) or at some remote location and the platform assembled at the site. Platform fabrication and equipment storage yards in the Gulf of Mexico and North Sea regions are large and require a waterfront location, perhaps at the expense of marine intertidal or subtidal habitats. Transportation of the platforms from the yards may require navigation channel widening, deepening or straightening. Similar navigational requirements may result from the greatly enhanced service vessel traffic which accompanies development and production. Transportation of oil and gas across coastal wetlands often entails dredging channels for laying pipelines. Dredging activities affecting coastal habitats are discussed in Chapter 13 and are not further described here.

Fluids and gases recovered from the well may include crude oil, natural gas, petroleum condensates, nonhydrocarbon waste gases, and water produced from the bearing formations. This complex mixture must be separated, either on the producing platform, a collector platform or ashore. Crude oil and condensates must flow in one stream, natural gas in another, waste gases vented or burned, and produced waters discharged or reinjected. The composition of produced waters is discussed in detail below.

Transport of oil and gas usually involves pipelines buried in the seafloor, except where economic conditions make this infeasible. Then, storage of the product offshore and onloading onto tankers or barges may be employed. All transport methods involve some risk of accidental spills; however, pipelines generally have a relatively safer record than vessel transport, particularly if offshore transfer to vessels is involved. The environmental effects of refinery operations are beyond the scope of this review because, at that stage, oil from numerous sources other than offshore production is refined. Because offshore oil and gas production in the U.S. satisfies only a small portion of the nation's demand and this condition is not likely to change, offshore discoveries and production are not likely to influence the distribution or expansion of refineries.

OPERATIONAL DISCHARGES

During well drilling and during production of oil and gas offshore, a wide variety of liquid, solid and gaseous wastes are produced on the platform, some of which are discharged to the ocean (Table 4.2). Such discharges are regulated by the Environmental Protection Agency (EPA) through issuance of National Pollutant Discharge Elimination System (NPDES) permits. Liquid and solid wastes that may be permitted for discharge to the ocean include cooling water

TABLE 4.2
Major permitted discharges and potential impact-causing agents associated with offshore oil and gas exploration and production

- Drill cuttings—1100 MT/exploration well, less for development well
- Drilling fluids—900 MT/exploration well, 25% less for development well
- Cooling water, deck drainage, ballast water—may be treated in an oil/water separator
- Domestic sewage—primary activated sludge treatment
- Sacrificial anodes, corrosion, antifouling paints—may release small amounts of several metals (Al, Cu, Hg, In, Sn, Zn)
- Produced water (production only)—treated in oil/water separator to reduce total HC to mean of 48 ppm, daily maximum 72 ppm

protected against biofouling and corrosion with antifouling paints and sacrificial electrodes. These may release small amounts of toxic heavy metals to the water column (Al, Cu, Hg, In, Sn, Zn) (Dicks, 1982). Produced water and oily wastes from deck drainage are passed through an oil-water separator, and domestic sewage is treated in an activated sludge treatment system before discharge. Treated waste water containing up to 48 ppm oil and grease is permitted for discharge to the ocean.

Drilling Discharges

The major discharges associated with exploratory and development drilling are drill cuttings and drilling fluids. Drill cuttings are particles of crushed sedimentary rock produced by the action of the drill bit as it penetrates into the earth. Drill cuttings range in size from clay to coarse gravel and have an angular configuration (as compared to the rounded shape of most weathered natural sediments). Their chemistry and mineralogy reflect that of the sedimentary strata being penetrated by the drill. Cuttings are considered relatively inert; nevertheless, they represent a potential input of trace metals, hydrocarbons and suspended sediments to the receiving waters, and, in addition, may account for continuous losses of small amounts of drill muds which are removed by normal cuttings washing procedures.

Drilling fluids are specially formulated mixtures of natural clays and/or polymers, weighting agents and other materials suspended in water or a petroleum material. Discharge to the ocean of water-based, but not oil-based, drilling fluids may be allowed by NPDES permit. Water-based drilling fluids (in which the major liquid phase is fresh or sea water) are used almost exclusively for drilling in U.S. coastal and outer continental shelf waters. In other parts of the world, such as the North Sea, oil-based drilling fluids are used frequently in offshore drilling operations.

Drilling fluids perform several functions integral to the rotary drilling process. The most important of these include transport of cuttings to the surface, balance of subsurface and formation pressures thus preventing a blowout, and cool, lubricate and support part of the weight of the drill bit and drill pipe. Drilling fluids are formulated to perform these functions optimally (McGlothlin and

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TABLE 4.3
Specialty additives and their functions in water-based drilling fluids (from Moseley, 1981)

Additive	Function	Concentration range in mud (g/l)	Frequency of use
...um bicarbonate	Eliminate excess calcium ions due to cement contamination.	0.3–11.4	very common
...um chloride	Minimize borehole washout in salt zone.	28.5–357	rare
...und nut shells,	Minimize loss of drilling mud to formation.	14.3–142	common
...ica or cellophane			
...ulose polymers	Counter thick, sticky filter cake; decrease filtrate loss to formation.	0.7–14.3	very common
...starch			
...minium stearate	Minimize foaming.	0.1–0.3	common
...alcohols	Reduce viscosity increase in high temperature wells—aid deflocculation capability of lignosulfonate.	0.3–5.7	rare
...um chromate	Reduce torque and drag on drilling string.	5.7–142	common
...sel or vegetable	Counter differential pressure sticking of drill string. Pill is placed downhole opposite contact zone to free pipe.	570–1140	common
...l lubricant			
...of oil-based mud			
...otting fluid	Retard bacterial degradation in polymer fluid systems. In development drilling, added to fluid left behind in casing to prevent casing string corrosion.	0.57–5.7	very common
...rmaldehyde			
...actericide			
...c compounds	Counter hydrogen sulfide contamination by precipitating sulfides.	1.4–14.3	common
...L-polymer drilling	Improve wellbore stability in water-sensitive shale formation. Prevents shale swelling and sloughing.	—	rare
...uid system			
...estos*	Improve solids carrying capacity; lift formation drill solids out of hole.	2.9–28.5	very rare

*...se prohibited in most OCS regions under EPA's NPDES program.

fluid and adjusts its composition to counteract changes in down-hole conditions. Thus, the composition of a drilling fluid is changed continually as the well is drilled. No two drilling fluids are identical in composition.

The five major ingredients in water-based drilling fluids (barite, clay, lignosulfonate, lignite and caustic) account for over 90% of the total mass of additives used in water-based drilling fluids (National Research Council, 1983). The other major ingredient is fresh water or sea water. There are more than one thousand additional tradename or generic materials available for drilling fluid formulation (World Oil, 1980). Most of these materials, however, are designed for use in oil-based muds and rarely more than 10 to 20 specialty additives are used to formulate a typical offshore water-based drilling mud.

Barite (barium sulfate) is used as a weighting agent in drilling fluids. It has a density of 4.1-4.3 g/cc and a solubility in sea water of about 50-52 µg/l as Ba (Burton *et al.*, 1968; Chan *et al.*, 1977). The amount of barite added to a drilling mud may vary from 0 to about 700 lb/bbl (0-2 kg/l) and usually increases with depth of the well (National Research Council, 1983).

Bentonite clay (sodium montmorillonite), or sometimes attapulgite clay, is the major ingredient of most water-based drilling fluids. It is used to maintain the gel strength required to suspend and carry drill cuttings to the surface. It also helps coat the wall of the bore-hole to prevent loss of drilling fluids to permeable formations.

Lignosulfonates are organic polymers derived from the lignin of wood and are byproducts of the wood pulp and paper industry. When complexed with certain inorganic ions such as chromium, iron or calcium, they are effective in preventing flocculation of clays. They are used to control the viscosity of drilling fluids. Chrome or ferrochrome lignosulfonate is used most frequently in water-based muds for offshore drilling. Lignite (a soft coal) is used with lignosulfonate as a clay deflocculant and filtration control agent.

Caustic (sodium hydroxide) is used to maintain the pH of drilling fluid in the range of 10 to 12. A high pH is needed for optimum clay deflocculation by chrome lignosulfonate and to inhibit corrosion of drill pipe and growth of hydrogen sulfide-producing bacteria.

Specialty chemicals, formulations and processes are used to solve particular technical problems encountered down-hole during the drilling operation. The most frequently used specialty chemicals, their functions and frequency of use are summarized in Table 4.3.

Several metals are found in drilling fluids (Table 4.4). The metals of major environmental concern, because of their potential toxicity and/or abundance in drilling fluids, include arsenic, barium, chromium, cadmium, copper, iron, lead, mercury, nickel and zinc. Some of these metals are added intentionally to drilling muds as metal salts or organometallic compounds. Others are trace contaminants of major drilling mud ingredients. The metals most frequently present in drilling fluids at concentrations significantly higher than in natural marine sediments include barium, chromium, lead and zinc (Table 4.4). Barium in drilling fluids is almost exclusively in the form of barite. Bentonite clay also may contain some

TABLE 4.4
Concentration ranges of several metals in drilling fluids from different sources and in typical marine sediments (concentrations in mg/kg dry wt, ppm)

Metal	Concentration in drilling fluids[1]	Concentration in marine sediments[2]
Barium	720–449,000	60–8100
Chromium	0.1–5960	10–200
Cadmium	0.16–54.4	0.3–1
Copper	0.05–307	8–700
Iron	0.002–27,000	20,000–60,000
Mercury	0.017–10.4	0.05–3.0
Lead	0.4–4226	6–200
Zinc	0.06–12,270	5–4000
Nickel	3.8–19.9	2–10 (10–1000)[3]
Arsenic	1.8–2.3	2–20
Vanadium	14–28	10–500
Aluminum	10,800	10,000–90,000
Manganese	290–400	100–10,000

[1] from Neff, 1982
[2] from Robertson and Carpenter, 1976
[3] deep-sea sediments

Chromium in drilling fluids is derived primarily from chrome and ferrochrome lignosulfonates. Different brands of chrome or ferrochrome lignosulfonate may contain from 1000 to 45,000 mg/kg chromium (Neff, 1982). Barite and lignite also may contain some chromium. In addition, inorganic chromate salts sometimes are added to drilling fluids for stabilization of chrome lignosulfonate at high temperatures, corrosion control, or H₂S scavenging. Frequently used offshore drilling fluids may contain 0.1 to about 1400 mg/kg dry weight, and exceptionally to 6000 mg/kg, total chromium. Chromium complexed to lignosulfonate is trivalent (Skelly and Dieball, 1969). Hexavalent chromium added to drilling muds is reduced quickly to the trivalent state by the lignosulfonate and other organic compounds in the mud, particularly at elevated temperatures. During use of a drilling fluid, the chrome lignosulfonate becomes adsorbed to the clay fraction (McAtee and Smith, 1969). Chrome-lignosulfonate-clay complexes are quite stable at normal operating temperatures. Above about 150°C, these complexes begin to break down due to thermal degradation of lignosulfonate.

Most of the other metals detected in some drilling fluids (mercury, lead, zinc, nickel, arsenic, cadmium and copper) are present primarily as trace impurities in barite, bentonite and sedimentary rocks in the formations penetrated by the drill. The average concentrations of these metals in marine sediments are as high as or higher, in most cases, than their concentrations in drilling muds (Table 4.4). The metallic impurities in barite are in the form of highly insoluble metal sulfides (Kramer et al., 1980; MacDonald, 1982). Mercury is of particular concern because of its high toxicity. Although mercury from mercuric sulfide can be

bacteria, the speed and efficiency of this transformation is only 10^{-3} times that of methylation of ionic Hg^{+2} (Fagerstrom and Jernelov, 1971) and the rate-limiting step appears to be oxidation of sulfide to sulfate (Gavis and Ferguson, 1972). This reaction will be oxygen limited in most marine sediments. Pipe thread compound (pipe dope) and drill collar dope may contain several percent metallic lead, zinc and copper (Ayers et al., 1980a). Some pipe dope gets into the drilling mud; however, metals from this source are in the form of fine metallic granules and are relatively inert biologically. Finally, inorganic zinc salts, such as zinc carbonate, zinc chromate or zinc sulfonate, may be added to drilling muds as H₂S scavengers. In such cases, zinc is precipitated as zinc sulfide.

The drilling fluid-handling system is an important part of any modern drilling rig and consists of several components (Figure 4.1). Drilling fluid is pumped under high pressure from the drilling fluid holding tanks on the platform down through the drill pipe and exits through nozzles on the drill bit. There it hydraulically removes cuttings generated by the grinding action of the drill bit. The drilling fluid, carrying cuttings with it, then passes up through the annulus (area between the drill pipe and the borehole wall or casing) to the drilling fluid return line. The drilling fluid passes through several screens and other devices which remove the cuttings from the fluid. The drilling fluid is returned to the holding tanks for recirculation down-hole, and the cuttings are discharged to the ocean.

During a normal exploratory drilling operation, several drilling fluid and cuttings-related effluents are discharged to the ocean. Typical discharges and discharge rates from an offshore platform are summarized in Table 4.5. The only, more or less, continuous discharge during normal drilling is of cuttings from the shale shakers. Although most of the drilling fluid is removed from the cuttings during passage through the shale shakers, discharged cuttings may contain 5 to 10% drilling fluid solids. Discharges of finer fractions of cuttings by the other solids-control equipment is more intermittent. The rate of cuttings discharge per day depends on the vertical distance drilled that day and the diameter of the drill hole. Hole diameter decreases in stages with depth from about 92 cm near the surface to about 16.5 cm at a depth of about 4600 m. Thus, the rate of cuttings discharge decreases as drill depth increases. In addition, drilling may actually occur only one-third to one-half the time during a two-three month drilling operation (National Research Council, 1983).

Whole used drilling fluids may be discharged intentionally in bulk quantities several times during a drilling operation. Small amounts (100-200 bbl; 15,900-31,800 l) of drilling fluid may be discharged to make space in the mud tanks for addition of water or drilling fluid ingredients added to change fluid properties. Changeover of mud programs, from one drilling fluid type to another, may require bulk discharge of most of the drilling fluid in the mud system. At the end of an exploratory drilling operation, most of the drilling fluid not left in the hole is discharged in bulk to the ocean. Bulk drilling fluid discharges may involve 1000-2500 bbl (159,000-397,500 l).

Unless restricted by NPDES permit, the rate of bulk drilling mud discharges ranges from 500 to 2000 bbl/h and may require 0.5 to 3 h (Ayers et al., 1980b;
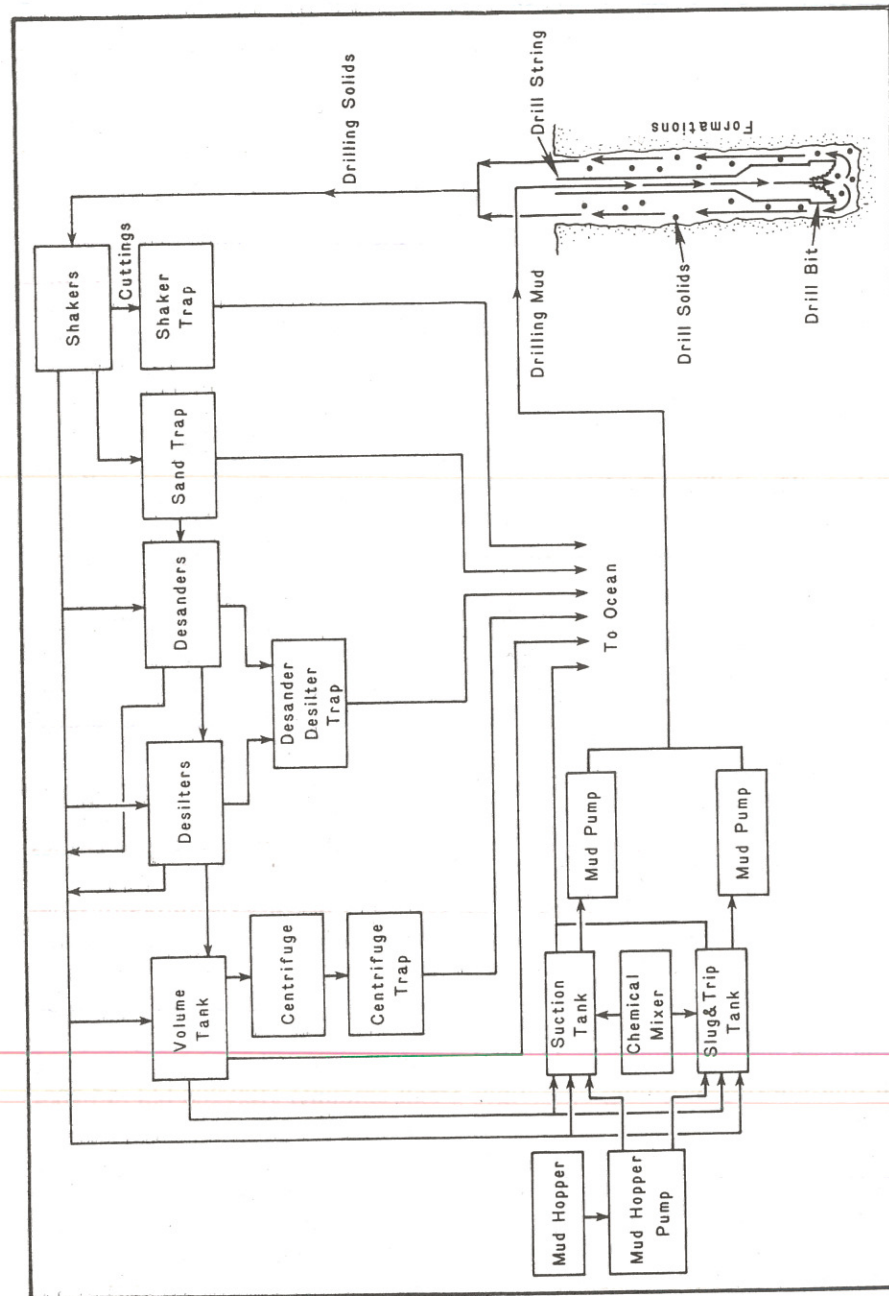
Figure 4.1. A generalized schematic diagram of the drilling fluid-handling system of an offshore oil rig (modified from Miller, 1983).

TABLE 4.5

Sources, discharge rates and discharge frequencies of continuous discharges of drilling fluids and drill cuttings (from Petrazzuolo, 1983)

Source	Rate (l/h)	Frequency
Shale shakers	160–320	Continuous during drilling
Desander	480	2–3 h/day during drilling
Desilter	2545–2700	2–3 h/day during drilling
Centrifuge	4770	1–3 h; every 2–3 days
Sand trap	87,500–420,000	2–10 min; every 2–3 days
Sample trap	240–480	5–10 min; every 2–3 days

Ray and Meek, 1980). Over the life of an exploratory well, from 5000 to 30,000 bbl of drilling fluids (200 to 2000 metric tons of solids) may be used. From 50 to 80% of this drilling fluid may be discharged to the ocean during or after drilling. Development wells, are usually shallower, smaller in diameter, and require less time to drill than exploration wells, and so the quantity of mud discharged per development well is usually somewhat smaller.

As many as 50 to 100 wells may be drilled from a single offshore development platform. After completion of each well, some of the drilling mud may be retained on board for use in drilling the next well. During drilling of a 10,000-ft (3048-m) production well, approximately 900 metric tons of drill cuttings will be generated and approximately 1000 tons of drilling fluid solids will be discharged. One or two wells at a time may be drilled from a development platform, each well requiring 2 to 6 months to complete. During the 4 to 20 years required to drill 50 wells from such a platform, approximately 95,000 metric tons of drilling fluid and cuttings solids would be discharged to the ocean.

Produced Water

Petroleum and natural gas may accumulate in commercial quantities where a layer of permeable sedimentary rock, such as sandstone or limestone, is sandwiched between layers of impermeable rock, such as shale, and lateral migration of the hydrocarbons is prevented by folding, faulting or salt dome intrusion of the sedimentary layers (Figure 4.2). Connate or fossil water (water that has been buried and out of contact with the atmosphere for at least a large part of a geologic period; White, 1957) may also accumulate in such reservoirs. Within the reservoir, natural gas accumulates at the shallowest depths, liquid petroleum is in the middle and water is at the greater depths. The relative proportions of the three materials may vary substantially in different reservoirs and one or more components may be absent.

During production of oil or gas, some of the connate water may be pumped up as well. This water is called formation water, produced water or oilfield brine effluent. Over the life of a well, the amount of water produced with the oil or gas often increases as the amount of oil produced decreases (Read, 1978). In older fields, production may be 95% water and 5% oil and gas.

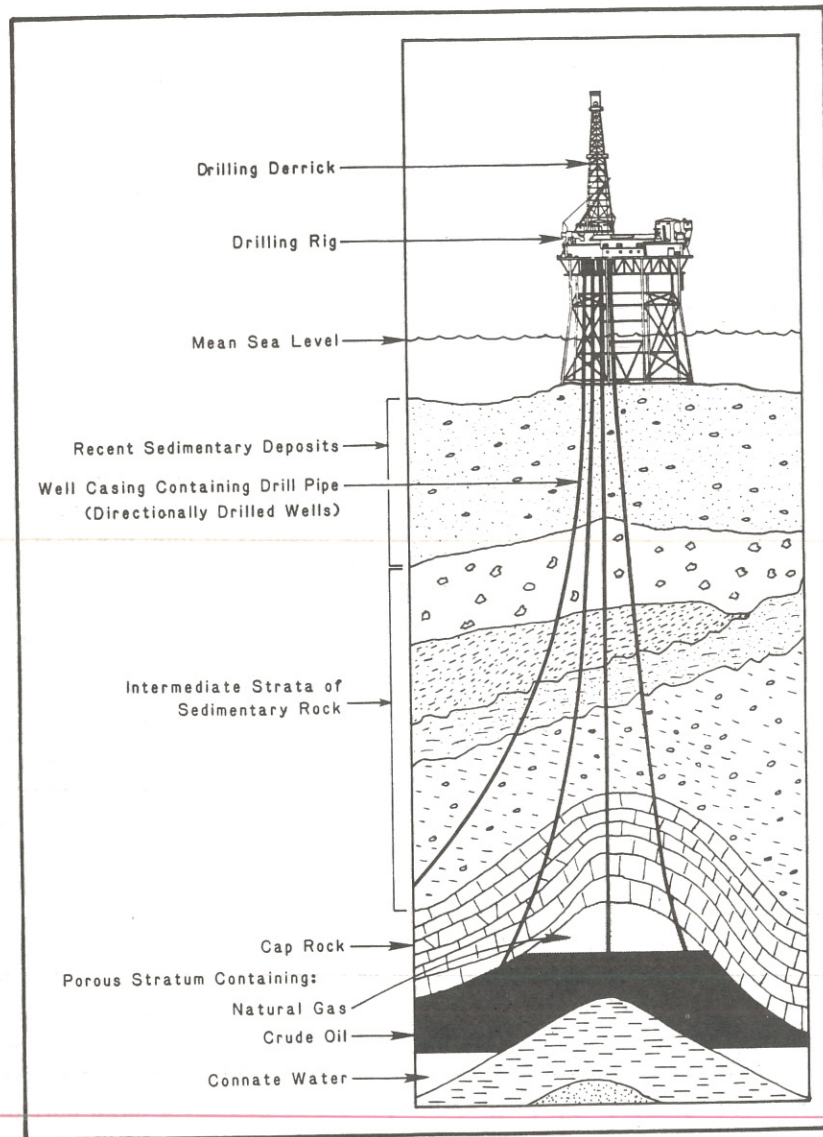Produced water may be reinjected into the reservoir to enhance recovery of

Figure 4.2. Schematic of an offshore development/production platform showing spatial relationship between the platform, drill string and the petroleum reservoir containing natural gas, crude oil and connate water.

the remaining hydrocarbons (secondary recovery), as a disposal mechanism for this potential pollutant or to control land subsidence. Surface fresh water or sea water also may be injected. In addition, water may leak into the well from shallower strata through a leaky casing or faulty completion. This water may find its way back to the surface as produced water. In 1970, daily production of

respectively (Collins, 1975). In the northwestern Gulf of Mexico, an estimated 47.7 million l/day of produced water were discharged to outer continental shelf waters. An additional 47 million l/day were being treated onshore and discharged to coastal waters (Brooks *et al.*, 1977). Discharges of treated produced water to Cook Inlet, Alaska from two onshore treatment plants (at Kenai and Trading Bay) and from one offshore production platform (Dillon) were estimated in 1981 at 12.9 million l/day (Lysyj, 1982). The produced water discharge from a single platform usually is less than about 1.5 million l/day, whereas discharges from large facilities handling several platforms may be as high as 25 million l/day (Menzie, 1982).

The concentration of total dissolved solids (salinity) in produced water from different locations in the United States and Canada ranges from less than 3 to about 300 g/l (parts per thousand) (Rittenhouse *et al.*, 1969). Most produced waters are more concentrated than sea water (35 ppt) and are thought to be of marine origin (Collins, 1975). They have an ionic composition similar to an evaporate of sea water, although actual ion ratios vary substantially depending on the geologic period from which they come and the chemistry of the sediments with which they are associated (Table 4.6). As in sea water, sodium and chloride are the most abundant ions, with some exceptions. The ratio of calcium to

TABLE 4.6

Concentrations of several elements in sea water and oil field waters of several geologic ages (Tertiary-Cambrian); concentrations in mg/kg (ppm) (data from Collins, 1975)

Element	Concentration in sea water	Concentration in oil field waters of different geologic ages	
		Highest (Age[1])	Range of means
Sodium	10,560	120,000 (J)	23,000–57,300
Chloride	18,980	270,000 (P)	46,100–141,000
Calcium	400	205,000 (P)	2530–25,800
Magnesium	1270	26,000 (D)	530–4300
Potassium	380	11,600 (D)	130–3100
Sulfate	880	8400 (T)	210–1170
Bromide	65	6000 (J)	46–1200
Strontium	8	4500 (P)	7–1000
Ammonium	—	3300 (P)	23–300
Bicarbonate	—	3600 (T)	77–560
Iodide	0.05	1410 (P)	3–210
Barium	0.03	670 (C)	5–60
Boron	4.8	450 (T)	8–40
Carbonate	—	450 (M)	30–450
Lithium	0.2	400 (J)	3–50
Manganese	0.002	200 (D)	12–175
Rubidium	0.12	11 (D)	0.1–4
Cesium	0.0005	8.5 (P)	0.1–0.6
Copper	0.003	3 (M)	0.6–3

C, Cambrian; D, Devonian; J, Jurassic; M, Mississippian; P, Pennsylvanian; T, Tertiary

magnesium concentration often is reversed compared to sea water. The concentration of elemental sulfur may be quite high. In produced water from the Buccaneer gas and oil field in the northwestern Gulf of Mexico, the maximum concentration of sulfur was 1200 ppm and the mean was 460 ppm (Middleditch, 1981b). Several potentially toxic metals may be present at elevated concentrations in some produced waters (Table 4.7). The accuracy of analyses by several investigators of the concentrations of metals in produced water from the Buccaneer field has been questioned by Middleditch (1984). Several of these values are out of the range of values reported by Collins (1975) for produced waters in general. Analysis of metals in concentrated saline brines by atomic absorption spectrophotometry is technically difficult because of significant matrix interferences. Much of the data for metals concentrations in produced water probably is unreliable. Based on the available analyses, metals that may be present in produced water at substantially higher concentrations than in sea water include barium, beryllium, cadmium, chromium, copper, iron, lead, nickel, silver and zinc.

Produced water may contain small amounts of radionuclides, primarily in the form of radium (^{226}Ra and ^{228}Ra). The radium apparently is derived from the normal concentrations of uranium and thorium associated with the clay minerals

TABLE 4.7
Concentration ranges of metals in sea water and in produced waters discharged to the Gulf of Mexico; concentrations in µg/kg (ppb)

Metal	Concentration in sea water[1]	Concentration in produced water general[2]	Concentration in produced water Buccaneer Field[3]
Antimony	0.5	—	0.061
Arsenic	3.0	0–10,000	0.32
Barium	10–63	to 100,000	6.4–3500
Beryllium	0.0005	20–200	0.25–2.7
Cadmium	0.11	0–1	0.057–32
Chromium	0.13–0.25	—	0.83–260
Copper	0.5–3.5	500–3000	0.55–120
Iron	1.7–150	trace–1,000,000	260–2900
Lead[4]	0.6–1.5	trace–100,000	0.78–760
Manganese	0.1–8.0	1000–6000	0.84–4.3
Mercury	0.15–0.27	0–150	0.16–0.4
Nickel	2.0	<1–15	0.35–1200
Silver	0.145	—	0.028–110
Strontium	8000	to 3,500,000	230–71,000
Thallium	0.01	—	0.33
Zinc	1.5–10	trace–500,000	15–610

[1] from Goldberg, 1963; Hood, 1963
[2] from Collins, 1975
[3] from Middleditch, 1984
[4] Patterson *et al.* (1976) report 0.02–0.10 ug/l total Pb for southern California coastal

and quartz sands that make up the matrix of the hydrocarbon/water reservoir (Reid, 1983). These radium isotopes are derived from radioactive decay of ^{230}Th and ^{232}Th. Radiodecay daughters of ^{226}Ra and ^{228}Ra of possible environmental interest include ^{210}Pb, ^{210}Po, and ^{228}Th and ^{224}Ra. In 32 samples of produced water from gas, oil and geothermal wells in coastal Louisana and Texas, Reid (1983) observed a direct correlation between salinity of the produced water (10–274 g/kg) and total radium concentration (30 to 2800 pCi/l) (Figure 4.3). Similar concentrations of radium have been reported in produced water from oil fields in the midwestern U.S. (Gott and Hill, 1953; Pierce *et al.*, 1955; Armbrust and Kuroda, 1956). However, there are no other data on radionuclide concentrations in produced waters from coastal and offshore waters of California and Alaska. The background concentration of total radium isotopes in coastal and marine waters is generally less than 1 pCi/l (Reid, 1983) or 2-17 x 10^{-14} g/l with concentration increasing with water depth (Szabo, 1967).

The U.S. EPA *Best Practicable Treatment Guidelines* restrict the concentration of oil and grease in produced water destined for ocean disposal to a monthly average of 48 ppm and a daily maximum of 72 ppm. New Source Performance Standards that have been proposed by the EPA include a daily maximum of 59 mg/l and a monthly average of 23 mg/l oil and grease (William Tilliard, EPA Washington, D.C., personal communication). The oil/water mixture produced from the well is either treated on the platform or transported to shore by pipeline to an onshore treatment plant. The oil and water phases are allowed to separate in a gravity separator and treated to remove additional dispersed oil before being discharged to the ocean or coastal waters. The produced water treatment system
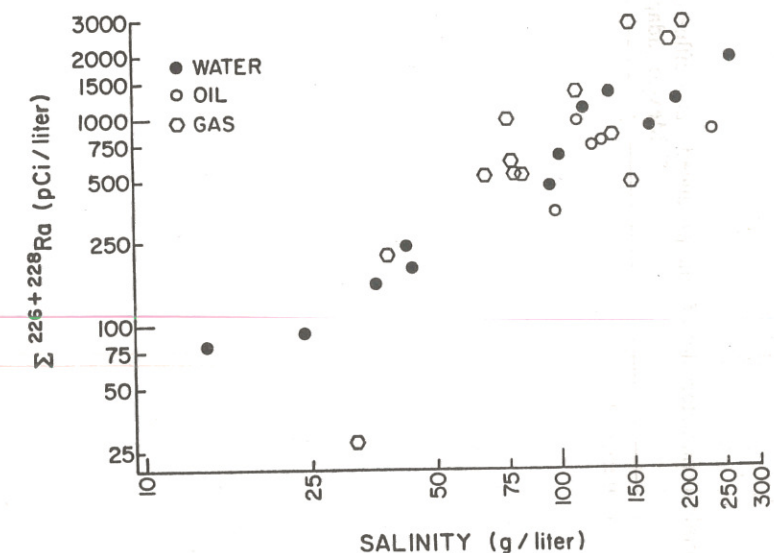

Figure 4.3. Relationship between total dissolved solids concentration (salinity) and concentration of total radium (Ra-226 plus Ra-228) in produced water from oil, gas and geothermal wells in Texas

is designed primarily to remove particulate or dispersed oil and therefore has little effect on the concentration of dissolved petroleum hydrocarbons, other organics and metal ions in the produced water (Jackson *et al.*, 1981; Lysyj, 1982). Concentrations of soluble nonvolatile organic compounds in produced water may be as high as 500-600 mg/l and they are not removed by conventional treatment methods (Lysyj, 1982). The composition of this organic material is not known. Some chemical and physical characteristics of treated produced water from 10 platforms in the northwestern Gulf of Mexico are summarized in Table 4.8. Produced water represented from 27 to more than 90% of total liquids produced by these wells. The pH of these waters was near neutrality and salinity

TABLE 4.9
Concentrations of selected petroleum hydrocarbons in produced water effluents from the Buccaneer platform in the northwestern Gulf of Mexico; concentrations in μg/l (ppb)

Compound	From Middleditch, 1981	From Sauer, 1981
Aromatic Hydrocarbons:		
Benzene	6100	1150
Toluene	5460	7460
Ethylbenzene	1200	850
m- *p-* and *o*-oxylenes		3570
Total C_3-Benzenes	24.2	5590
C_4-Benzenes	22.2	830
C_5-Benzenes	4.5	NA*
C_6-Benzenes	3.2	NA
C_7-Benzenes	0.9	NA
C_8-Benzenes	1.2	NA
C_9-Benzenes	2.4	NA
C_{10}-Benzenes	1.0	NA
C_{11}-Benzenes	0.3	NA
Naphthalene	11.1	170
Methylnaphthalenes	7.2	20
C_2-Naphthalenes	10.4	NA
C_3-Naphthalenes	4.3	NA
C_4- and C_5-Naphthalenes	0.9	NA
Biphenyl or Acenaphthene	2.8	NA
C_1- and C_2-Biphenyls	2.9	NA
Alkanes:		
C_1–C_{13}	3120	3100
Cycloalkanes	2580	1060
Alkenes	580	NA
C_{14}–C_{29}	1476	NA
Total Aromatics Measured	12,860	16,070
Total Alkanes Measured	4596	3170
Total Cycloalkanes Measured	2580	1060
Total Alkenes Measured	580	NA
Total Hydrocarbons Measured	20,616	20,300

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TABLE 4.8
...e chemical characteristics of final produced water effluents from production systems on 10 offshore production platforms in the Gulf of Mexico (adapted from Jackson *et al.*, 1981)

Parameter	Platform 1	2	3	4	5	6	7	8	9	10
...er cut, percent	35	64	47	27	32	91	87	10	90	19
...uced water properties										
...H	6.9	7.0	6.3	6.6	6.3	6.7	6.6	7.1	6.3	6.2
...tal dissolved solids (g/l)	105	80.5	203	114	138	108	112	114	162	163
...pecific gravity	1.086	1.073	1.151	1.093	1.129	1.095	1.095	1.106	1.140	1.133
...urface tension (dynes/cm)	67	60	67	60	61	61	63	66	57	68
...concentration (mg/l ± S.D.)										
...y Gravimetric	77 ± 73	63 ± 95	64 ± 74	22 ± 6.7	12 ± 13	26 ± 6.9	7.6 ± 5.2	18 ± 9.2	52 ± 24	48 ± 16
...y Infrared	106 ± 99	81 ± 109	95 ± 103	39 ± 4.2	37 ± 19	36 ± 8.3	15 ± 3.7	36 ± 7.8	76 ± 38	48 ± 16
...Dispersed Oil"	38 ± 80	66 ± 106	92 ± 126	4.9 ± 5.1	5.9 ± 13	26 ± 8.6	1.6 ± 1.5	5.7 ± 7.7	63 ± 30	23 ± 13
...Soluble" Oil"	61 ± 15	30 ± 32	21 ± 13	36 ± 4.1	28 ± 3.1	10 ± 2.3	13 ± 2.7	31 ± 2.7	13 ± 13	25 ± 4.7
...Soluble" Oil as Percent IR Oil	58	37	22	92	76	28	87	86	17	52

ranged from 80 to 203 ppt. The concentration of total oil by infrared analysis ranged from 15 to 106 mg/l (ppm) and was quite variable from platform to platform and from a single platform over time. The concentration of oil in solution or colloidal suspension ranged from 10 to 61 ppm.

The solubility of petroleum hydrocarbons in sea water decreases logarithmically as hydrocarbon molecular weight increases (McAuliffe, 1966). Aromatic hydrocarbons are more water soluble than aliphatic hydrocarbons of similar molecular weight. Therefore, the soluble fraction of oil in produced water is greatly enriched in light aliphatic and especially aromatic hydrocarbons compared to the dispersed oil fraction (Neff and Anderson, 1981). Hydrocarbons in produced water from the Buccaneer gas and oil field in the Gulf of Mexico

TABLE 4.10

Hydrocarbon composition of oil from the C-2 separator platform, Trinity Bay, Texas, full strength effluent from the C-2 separator platform, water collected near the bottom at station 1 and bottom sediment at station 1 (from Armstrong *et al.*, 1979)

Compound	Oil (%)	Produced water effluent (ppm)	Water (ppb)	Sediment (ppm)
Alkanes:				
Total C_7–C_{31}	25.03	13.43	0.00	61.90
Aromatics:				
Benzene	1.27	3.30	1.5	—
Toluene	1.22	3.50	3.2	—
Xylene	1.60	2.40	*	—
C_2-Benzene	—	—	3.1	—
C_3-Benzene	1.00	0.65	0.8	0.6
C_4-Benzene	—	—	—	0.4
Naphthalene	0.21	0.30	0.4	0.2
1-Methylnaphthalene	0.29	0.37	0.2	0.5
2-Methylnaphthalene	0.39	0.50	0.6	0.5
Dimethylnaphthalenes	1.24	0.03	*	0.8
Trimethylnaphthalenes	1.52	0.26	*	10.0
C_4-Naphthalenes	—	—	—	0.4
Biphenyl	0.03	0.015	*	*
Methylbiphenyls	0.06	0.011	*	0.2
Dimethylbiphenyls	0.01	0.03	*	0.8
Fluorene	0.01	0.014	*	0.1
Methylfluorenes	0.07	0.063	*	0.7
Dimethylfluorenes	0.04	0.042	*	0.9
Trimethylfluorenes	—	—	—	0.6
Phenanthrene	0.02	0.036	*	0.1
Methylphenanthrenes	0.05	0.063	*	0.6
Dimethylphenanthrenes	0.03	0.020	*	1.0
Trimethylphenanthrenes	—	—	—	0.5
Total Aromatics	9.06	11.76	10.50	34.20
Total Hydrocarbons				
Measured	34.09	25.19	10.50	96.10

were dominated by monoaromatic hydrocarbons and light alkanes (Table 4.9). Naphthalenes were present in trace amounts, and higher molecular weight aromatics were not measured. Middleditch (1981) estimated the concentration of benzo(a)pyrene in produced water at 1 to 5 µg/l, somewhat in excess of its estimated solubility in sea water: 0.1 to 1.0 µg/l (Neff, 1979).

Produced water from a separator platform in Trinity Bay, Texas contained traces of phenanthrenes (Table 4.10). The C_{14}-C_{29} alkanes and high molecular weight aromatic hydrocarbons probably were present primarily in the dispersed phase of the produced water, since they are virtually insoluble in sea water. Other organics sometimes encountered in produced waters include ketones (from solvents used to clean rig structures), phenols and organic acids from the produced water and biocides used to inhibit hydrogen sulfide, sulfuric acid and scale formation in the production system (Collins, 1975; Middleditch, 1981). The estimated amount of petroleum hydrocarbons in produced water discharged to the British and Norwegian sectors of the North Sea in 1978-1980 was 1435 metric tons/year (Read, 1978; Schreiner, 1978). The National Research Council (1985) estimated that the worldwide input of petroleum hydrocarbons from produced water discharges to be between 7500 and 11,500 metric tons per year, with about one-fourth of this in U.S. waters.

Deck drainage, which may contain a variety of chemicals such as detergents, solvents and metals, is processed through the oil/water separator before discharge to the ocean. In addition, a wide variety of chemicals may be added to the process stream of the oil/water separator and ultimately appear in the effluent water (Middleditch, 1984). These may include biocides, coagulants, corrosion inhibitors, cleaners, dispersants, emulsion breakers, paraffin control agents, reverse emulsion breakers, and scale inhibitors. The concentrations of these materials in produced water effluent are not well known.

OIL SPILLS

Offshore oil and gas development carries with it the risk of oil spills at the platform and in transporting the oil from the platform to shore. Spills at the platform result from leaks or blowouts during both exploratory and production drilling. Most oil and gas produced offshore is transported ashore through pipelines. Oil spills result from pipeline ruptures or chronic leaks. Where technologically difficult or economically infeasible, transport of oil by pipelines is replaced by storage of the product offshore, then transfer to tankers or barges. This method is commonly viewed as less safe than pipelines in that it creates an increased risk of oil spills, both acute spills and chronic inputs.

Lanfear and Amstutz (1983) presented data on accidental spills on the U.S. outer continental shelf (OCS). Although they provided analyses based only on spills of 1000 bbl or greater, the values allow for comparison of the rates of occurrence of the above mentioned types of oil spills associated with offshore development. The average spill rate for OCS platforms from 1964 to 1980 was 2.05 spills per billion barrels produced. The comparable value for spills for

TABLE 4.11

Transportation modes and large spill information for U.S. OCS planning areas based on unleased resources as of July 31, 1986 (adapted from Department of Interior, 1985)

Planning area	Undiscovered recoverable oil risked mean estimated (billion bbl)	Transportation mode (P, pipelines; T, tankers)	Probability of spill reaching land	Expected number of spills >1000 bbl Occurring	Reaching shore	Estimated spills reaching shore (bbl)
Central Gulf of Mexico	2.05	P/T	0.772	5.94	4.59	131,743
Western Gulf of Mexico	1.55	P	0.728	4.03	2.93	98,451
Southern California	1.23	P/T	0.500	2.30	1.15	69,766
Central California	0.36	P/T	0.444	1.84	0.82	21,032
Navarin Basin	0.45	P/T	0.150	2.87	0.43	76,851
Beaufort Sea	0.41	P/T	0.231	1.99	0.46	40,286
Chukchi Sea	0.40	P/T	0.225	1.75	0.39	39,195
Northern California	0.25	P/T	0.444	1.84	0.82	14,597
Eastern Gulf of Mexico	0.25	P/T	0.432	1.21	0.52	33,839
North Atlantic	0.13	P/T	0.039	0.63	0.02	17,661
St. George Basin	0.07	P/T	0.144	0.66	0.10	9572
Mid-Atlantic	0.04	T	0.106	0.37	0.04	3359
South Atlantic	0.02	P/T	0.100	0.16	0.02	1960
North Aleutian	0.01	P/T	0.342	0.16	0.05	893
Washington-Oregon	0.01	T	—	0.09	0.09	1306
Gulf of Alaska	0.01	P/T	0.851	0.10	0.09	496
Norton Basin	0.01	P/T	0.250	0.06	0.02	496
Kodiak	0.01	P/T	0.545	0.04	0.02	0
Hope Basin	negl.	P	NA	negl.	negl.	0
Shumagin	negl.	P	NA	negl.	negl.	0
...st of Alaska	negl.	P	NA	negl.	negl.	0

for tanker accidents involved in transshipment to shore; however, one for general maritime transport of oil (3.87 spills per billion barrels transported) indicates that tanker transport creates a greater risk of oil spillage than pipelines. If those spills which occurred in harbors or piers are deleted from the analysis (i.e., less representative of those subjected to OCS winds and currents), then the expected spill rate for worldwide tanker accidents for 1974-1980 is 1.3 spills per billion barrels transported. The evidence now points to a sharp drop in oil spill occurrences from production platforms and tankers since 1974 (Lanfear and Amstutz, 1983). This better safety record could result from a number of factors—greater industry concern, increased public pressure, stricter government regulation, and better technology.

Large spills from OCS production are rare. No spills over 1000 bbl have occurred since 1981, and only three such spills since 1979 (Department of Interior, 1985). Nonetheless, large spills do occur, and the potential for damage from such spills is serious. The reduction in the oil spill rate since 1974 (Lanfear and Amstutz, 1983) and availability of data for spills >1000 bbl has made it difficult to predict spill rates needed in oil and gas resource management decisions. Nonetheless, based on the available data and models, predictions have been made for the various OCS regions (Table 4.11).

Although the number of small spills is larger, the total amount of oil from these is relatively small compared to the total amount attributable to large spills. For example, 934 small spills (<1000 bbl) constituted >99% of all production platform and pipeline incidents recorded in the Gulf of Mexico from 1974 to 1983 (Department of the Interior, 1985). Yet, these spills accounted for only about 28% of the volume of oil spilled during the period.

Based on new estimates by the National Research Council (1985), offshore oil and gas development contributes only a very small fraction of the petroleum entering the marine environment (Table 4.12). Other sources include river and terrestrial runoff from municipal, urban and industrial sources, natural seeps and atmospheric transport. A significant source is bilge cleaning of tankers.

Of the 0.04 to 0.07 x 10^6 metric tons per annum (mta) attributed to offshore production, major spills (>7 metric tons) contributed 0.03 to 0.05 x 10^6 mta, minor spills (<7 metric tons) 0.003 to 0.004 x 10^6 mta, and operational discharges 0.007 to 0.011 x 10^6 mta (National Research Council, 1985). Less than 0.01% of worldwide offshore petroleum production (658 x 10^6 mta in 1979) is accidentally spilled or operationally discharged into marine waters (Koons, 1984; National Research Council, 1985).

A compilation of minor crude oil spills by the U.S. Geological Survey for Gulf of Mexico OCS oil and gas operations indicates that 0.00024% of the total crude oil produced was spilled between 1971 and 1978. The spill rate for Lower Cook Inlet was less (0.0001%). Although similar data are not available for other U.S. areas, the spill rates are expected to be comparable. As offshore operations move into more severe environments, such as the Arctic, or into deeper waters, the incidence of minor spills may increase. On the other hand, technological advances, such as warning systems and improved blowout preventers, will help

TABLE 4.12

Input of petroleum into the marine environment. Units are 10^6 metric tons per annum (adapted from National Research Council, 1985)

Source	Probable range	Best estimate	Percentage of total
Natural Sources (Marine seeps, sediment erosion)	0.025–2.5	0.25	7.7%
Offshore Production (Spills and operational discharges)	0.04–0.06	0.05	1.5%
Transportation (Tanker operations, dry-docking, marine terminals, bilge and fuel oils, tanker accidents, non-tanker accidents)	0.95–2.62	1.47	45.2%
Atmosphere	0.05–0.5	0.30	9.2%
Municipal and Industrial Wastes and Runoff (Municipal wastes, refineries, non-refining industrial wastes, urban runoff, river runoff, ocean dumping)	0.585–3.12	1.18	36.5%
Totals	1.7–8.8	3.25	

The spill rate for major spills in the Gulf of Mexico OCS for the same period as above was 0.002% of the oil produced per year. This average is assumed to apply nationwide. Worldwide, however, the spill rate, with the exception of the United Kingdom, is probably higher. This assumption is based on less restrictive regulation of blowout prevention outside of the U.S. and United Kingdom.

Major spills which occur outside U.S. territorial waters were not included in these estimates, but as shown by the IXTOC-I spill, can be of consequence to U.S. coastal and offshore environments. A blowout occurred on an exploratory well, IXTOC-I, in the Bay of Campeche, Mexico in June 1979. Before capping of the well in March of the next year, an estimated 454 x 10^3 to 1.4 x 10^6 tons of oil were spilled (Atwood, 1981; Teal and Howarth, 1984; National Research Council, 1985). Oil reached both Mexican and Texas beaches. It was estimated that 10^5 tons of oil came ashore in Texas. Less than 10% of the oil from the blowout was recovered.

Even those areas free of oil exploration and production activity are subject to potential pollution resulting from petroleum transportation. A large portion (45.3%) of the petroleum entering marine waters is from this source which includes tanker operations, dry docking, marine terminals, bilge and fuel oils from all ships, and accidental spills from tankers and nontankers (Table 4.12). Discharges and accidents are, of course, more likely to occur in the normal

The number of individual hydrocarbon components which enter the marine environment as a result of spills is quite large. The chemical composition of crude oils is complex and varies among different producing regions and even within a formation. A summary of the chemical composition of hydrocarbon sources is provided by the National Research Council (1985). Specific examples related to fates and effects of these hydrocarbons are provided in greater detail in Chapters 5, 6, 7, and 8.

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